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Reorientation of the Ce–D pairs in a $Pd_{95}Ce_5D_n$ alloy

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Abstract

Internal friction measurements have been carried out in a $Pd_{95}Ce_5$ alloy containing different amounts of D ($0.003<n_D=D/(Pd+Ce)<0.335$) at vibration frequencies in the kHz range. Three IF peaks P_1, P_2 and P_3 have been observed at around 160, 115 and 103 K, respectively. The highest temperature peak P_1 is due to D-dislocation interactions (Snoek-Koester type of relaxation), the peak P_2 to stress-induced reorientation of Ce–D pairs and the peak P_3 is due to stress-induced changes in the short-range order of D within the sublattice of the octahedral interstitial sites (Zener type of relaxation). The relaxation parameters of peak P_2 are: $\tau_0^{-1}=7\times10^{12}$ s^{-1} and $W=0.22$ eV, while an estimate of the anisotropy factor for the Ce–D pairs gives a value of 0.038.

Keywords: Mechanical relaxation; Elastic properties; Lattice defects; Pd–Ce alloys

1. Introduction

It is well known that hydrogen and deuterium may interact with substitutional atoms in dilute alloys giving rise to diatomic complexes, both in bcc and fcc lattices [1–8]. Ni-, Fe- and Co-based alloy systems have been most extensively investigated, either by magnetic disaccomodation or internal friction (IF) techniques. Recently, also, Pd containing Y as a substitutional impurity has been found to display an internal friction relaxation which has been attributed to reorientations of Y–H pairs [9,10].

Cerium atoms are expected to behave similarly to Y atoms when in solution in the Pd lattice; thus, they should both give rise to the formation of pairs with H(D). However, the form of pressure-composition isotherms at room temperature suggests that for the case of Ce as a solute the impurity–H(D) binding enthalpy is very small; thus, the question arises whether this impurity dissolved in Pd may actually constitute a trapping centre for H(D) [11,12]. The aim of the present work was to detect IF peaks due to Ce–D pairs in Pd.

2. Experimental

The alloy used in the present work was prepared by arc-melting 99.95% pure Pd with 99.9% pure Ce under an argon atmosphere. The button was rolled and machined to obtain bars of $0.54\times6.95\times44.6$ mm^3 dimensions, which were then annealed in vacuo ($P=4\times10^{-6}$ torr) at about 1300 K for 3 h. The doping of the samples with deuterium was carried out at temperatures ranging between about 400 and 500 K in a D_2 atmosphere at gas pressures of between 150 and 700 torr and with doping times of between 1 and 2 h. Deuterium contents n ($n=D/(Pd+Ce)$) were determined gravimetrically with an accuracy better of than 0.001.

The internal friction measurements were carried out by monitoring the number of oscillations included between two fixed amplitude levels during the free decay of the vibrations of the sample, which had been initially excited in one of its free–free resonant modes. All the data were taken at an average cooling rate of approximately 5×10^{-3} K s^{-1}.

3. Results

The temperature dependence of the elastic energy dissipation coefficient Q^{-1} and of the Young's modulus E for a specimen charged with gradually increasing deuterium contents n_D ($n_D=D/(Pd+Ce)$) is shown in Fig. 1a Fig. 1b Fig. 2, respectively. At deuterium levels $n_D\leq 0.007$ a single peak (P_2) occurs (see Fig. 1a) at a temperature T_{2M} which remains constant with changing D content ($T_{2M}=115$ K). For $0.007<n_D<0.05$ the IF shows two closely spaced bumps and the temperature of the

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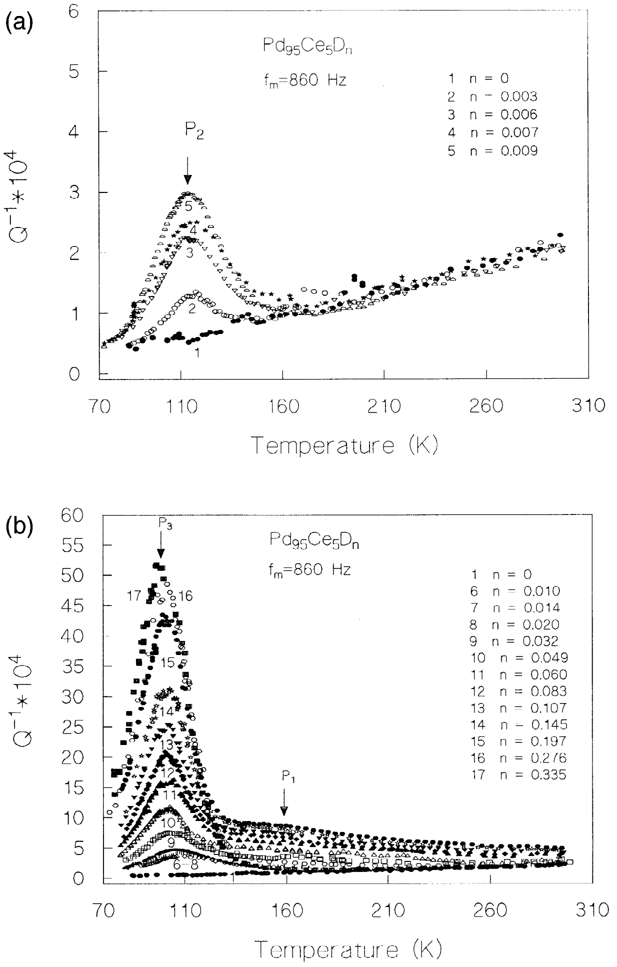

Fig. 1. (a) Internal friction spectra for a $Pd_{95}Ce_5$ alloy charged with deuterium contents $n \leq 0.009$ ($n = D/(Pd+Ce)$) as measured during cooling at a vibration frequency of about 890 Hz. The peak labelled P_2 corresponds to Ce–D pairs. (b) As (a) but for higher deuterium contents. The peaks labelled P_1 and P_3 correspond to Snoek-Koester and Zener relaxations, respectively.

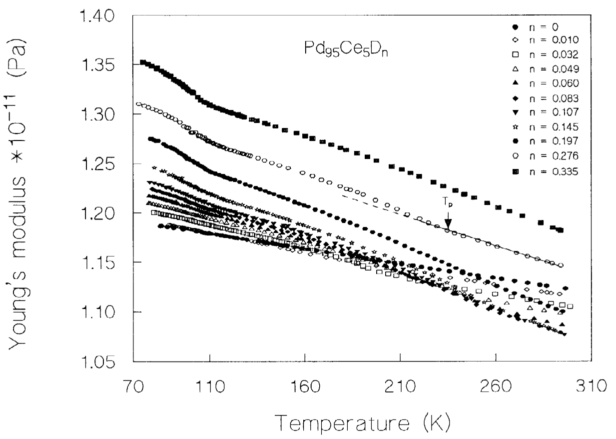

Fig. 2. Young's modulus vs. temperature curves for a $Pd_{95}Ce_5$ alloy charged with different amounts of deuterium, as measured during cooling at a vibration frequency of about 890 Hz. Onsets of precipitation of α' deuteride are revealed by departures from linear behaviour of $E(T)$ curves at the temperature T_p.

composite peak decreases down to 102 K with increasing D content. For $n_D > 0.05$ the temperature of this peak remains constant indicating a well-defined structural mechanism for the relaxation, which is now labelled as relaxation P_3 (see Fig. 1b). For $0.02 \leq n_D \leq 0.197$ a broad third peak (P_1) occurs at temperatures $(T_{1M}) \cong 160$ K. This peak has disappeared at the highest n_D contents of 0.276 and 0.335.

The height (Q_{2M}^{-1}) of the relaxation peak P_2, after correction for background, initially exhibits a linear increase with increasing n_D up to a value equal to about 0.01 and then tends to saturate (see Fig. 3). This behaviour is consistent with D being trapped by Ce. The relaxation parameters τ_0^{-1} and W, as deduced from an Arrhenius type of plot, turn out to be 7×10^{12} s^{-1} and 0.22 eV, respectively. The inverse of the limiting relaxation time is of the right order of magnitude for a jumping point defect, while the activation energy W is about the same as that reported in the literature for deuterium diffusion within the solid solution (α phase) of P_d [13]. The width of peak P_2 is about three times larger than that of a single time relaxation indicating that the process is associated with a wide spectrum of relaxation times.

The form of the temperature dependence of Young's modulus (Fig. 2) clearly shows the presence of relaxation processes P_2 and P_3 at around 110 K, while peak P_1 is too broad to be clearly distinguished in these plots. For deuterium contents n_D higher than about 0.02 rather steep changes in the $E(T)$ curves are observed at temperatures T_p, which are dependent on n_D. Such changes in the temperature coefficient of $E(T)$ curves may be expected to correspond to the onset of precipitation of the α' deuteride phase. The boundary of the regions of coexistence of the α-phase D solid solution and the α'-phase as deduced from the $T_p(n_D)$ dependencies are shown in Fig. 4. From this plot a critical temperature T_c of about 275 K and a critical concentration n_c of about 0.14 have been deduced for the $Pd_{95}Ce_5D_n$ alloy.

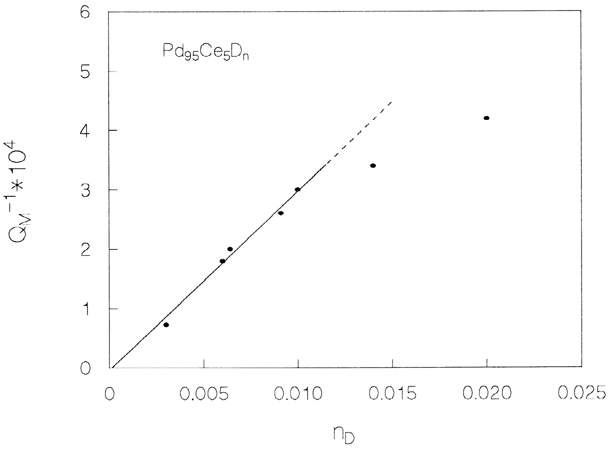

Fig. 3. The dependence on deuterium content n_D ($n_D = D/(Pd+Ce)$ at.) of the height Q_M^{-1} of the relaxation process P_2 due to stress-induced Ce–D pairs.

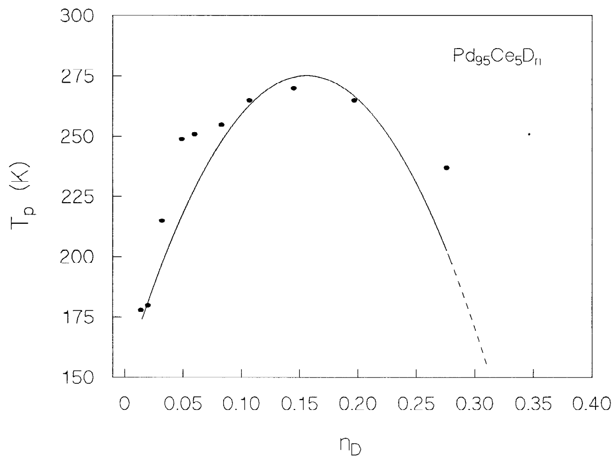

Fig. 4. A portion of the phase diagram of the $Pd_{95}Ce_5D_n$ alloy as deduced from the anomaly observed in the temperature dependence of $E(T)$ curves of Fig. 1b.

4. Discussion and conclusions

4.1. Young's modulus data and phase diagram of the $Pd_{95}Ce_5D_n$ system

Although the investigation of the phase diagram of the Pd–Ce–D ternary system was not one of the main goals of the present work, it is, nonetheless, of interest to briefly discuss the observations made with regard to the boundaries of the coexistence region of the α and α' phases, since these have not been previously determined at low temperatures. It is noteworthy that the corresponding critical temperature has been markedly decreased (from $\cong$565 K for the Pd–H system [11–13] down to about 275 K) by the addition to Pd of 5% Ce, similar to what happens when Pd is alloyed with other lattice-expanding substitutionals, such as Ag [13]. It would seem likely that this depression of the critical temperature for the PdCeD alloy system is a consequence of changes in the long-range elastic H–H interactions, which could also be responsible for the enhanced solubility limit within the α-phase.

4.2. IF peaks

The internal friction spectra of the $Pd_{95}Ce_5D_n$ alloy is similar to that for $Pd_{1-x}Y_xH_n$ alloys [9,10] and, to some extent, to that of the PdD(H) [14] and PdAgD(H) systems [15]. Thus, interpretations similar to those outlined in previous works [14,15,9,10] would also seem applicable to the present case. Accordingly, the peak P_1 would be due to interactions of deuterium atoms with misfit dislocations introduced by precipitation and dissolution of the α'-phase during cooling and heating (Snoek-Koester relaxation) [16], the peak P_2 would be due to the stress-induced reorientation of Ce–D pairs, and the peak P_3 would be due to stress-induced changes in the short-range order within the concentrated α'-phase (Zener effect) [14].

4.2.1. P_1 relaxation

It is by now well established that dislocations, either introduced by cold-work subjected to the sample prior to D loading or introduced during heating and cooling of the material through $\alpha+\alpha'$ coexistence regions, can drag with them clouds of D(H) mobile impurities giving rise to an anelastic process, the relaxation time and strength of which are controlled by the mean length of the dislocation segments and by the density of the impurity clouds. From previous work it had already been inferred [14] that the active dislocations are those moving within the dilute α-phase hydrogen solid solution region. Strong evidence in support of this assumption is provided by the data in Fig. 1a, which show complete disappearance of peak P_1 at D contents larger than 0.197, that is, when the sample is in a situation of homogeneous α'-phase over the entire temperature range. It may be again noted that the peak P_1 is extremely broad, indicative of a wide spectrum of relaxation times, and, correspondingly, of dislocation lengths and densities of D clouds around the dislocations.

4.2.2. P_2 relaxation

The linear relationship between

Q_M^{-1}

and n_D for values of $n \leq 0.01$ suggests that this relaxation is associated with stress-induced reorientation of Ce–D pairs and, furthermore, that structures of these pairs are not basically changed by changing D content. In apparent contrast with this clear indication of a well-defined unique structural mechanism for the relaxation, the existence of a wide spectrum of relaxation times would suggest a relatively complex microscopic situation. In order to identify the source of this spectrum of times it is useful to take into account data available in the literature for the Pd–Y–H system [10], for which the width of the spectrum of relaxation times was found to increase with increasing Y content, thus indicating strong interactions among Y–H pairs and isolated Y atoms. Therefore, even though the present experiments have been carried out only for a single Ce composition, it seems reasonable to attribute the spectrum of times of P_2 to internal stresses produced by isolated Ce atoms.

On the basis of room-temperature solubility data the binding energy of Ce–D pairs should be smaller than $kT \cong 0.03$ eV [12] and fractions of trapped D atoms at $n_D \ll n_{Ce}$ may depart from unity even at the relatively low temperatures of peak P_2. However, assuming that the concentration of pairs coincides with the overall D content n_D, as has been done by Kronmüller et al. [10], should not introduce big errors into the calculation of the relaxation strength Δ per unit concentration of the relaxing defect. Then, assuming a Gaussian distribution for the relaxation times and a <100> tetragonal symmetry for pairs, which implies occupancy by D of octahedral sites nn in relation to the Ce atom, the anisotropy factor $|\lambda_2 - \lambda_1|$ can be deduced from the following relation which is valid for polycrystalline samples vibrating in flexion [10]

$$\Delta \cong \frac{Q_M^{-1}}{f(0,\gamma)} \cong \frac{4}{45}\frac{\nu_0}{kT}E(\lambda_2 - \lambda_1)^2 \qquad (1)$$

where, $f(0,\gamma)$ is a function given by Berry and Nowick [17] which accounts for the width of the Gaussian spectrum ($f(0,\gamma) \cong 0.19$ for the present case); ν_0 is the atom volume of the host lattice and $\lambda_{1,2}$ are the principal components of the λ tensor [17]. From Eq. (1) we get a value of 0.038, a value which is about the same as the one (0.037) that has been deduced for the Y–H pair [10].

At the end of this discussion we should mention that in the ordered LI2 structure of the PdY3 system neutron diffraction data suggest preferential occupancy by H of interstices surrounded by six Pd atoms, rather than by four Pd and two Y atoms [16]. At first sight this finding might raise some doubts about the actual tendency of H to form Y–H pairs (and, by analogy, Ce–H pairs), which is, to some extent, in contrast with the interpretation of anelasticity data. However, the two sets of data, in our view, are not in contradiction with one another, but rather they simply reflect differences in the affinities with Y(Ce) of H either in solution in the ordered or in the disordered structures of the Pd–Y (Pd–Ce) system.

4.2.3. P_3 relaxation

By analogy with a relaxation investigated in detail in the case of the PdD(H) system [14] peak P_3 is to be attributed to stress-induced changes in the directional short-range order of D atoms over the sub-lattice of octahedral interstitial sites. According to this assignment the temperature of the peak should remain constant over the region of coexistence of the α and α'-phases, that is, for D contents $0.01 < n_D < 0.30$. In this same interval of contents the strength of the relaxation should be expected to increase linearly with n_D. These expectations are substantially in agreement with the experimental results, except for the fact that the peak temperature actually remains constant only beyond $n_D \cong 0.05$. This happens to some extent also with the PdD(H) system [14] and seems likely to be a manifestation of a D concentration within the hydride precipitates which changes with alterations of the overall D content.

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